ANCHORED ORGANIC AND INORGANIC COMPOUNDS ON GRAPHENE FRAMEWORK AS MATERIALS FOR SENSING AND ENERGY APPLICATIONS

PhD Synopsis submitted to CHRIST (Deemed to be University)
as partial requirement for the award of the Degree of

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

by

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July 2020

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Abstract

The specific atoms or group of atoms that can attach to the other organic or inorganic compounds due to the strong affinity is called as the anchoring group. The electrons from these organic and inorganic compounds are potent to travel through the anchor group. This leads to specific features with the change in the arrangement of atoms in the entire molecule/system. Hence, the redox reaction properties, molecular chain length and the extent of conjugation of the resultant anchored product vary. Depending upon the binding nature, anchoring groups can be divided into monodentate, bidentate, and multidentate. Among these, multidentate anchoring groups are more significant since it can bind either partially to the molecules or with the whole surface. Though many multidentate anchoring groups like fullerene, carbon nanotubes, polymers, calixarenes, and graphene are presented in the literature, graphene oxide anchored organic and inorganic compounds are important because of its amazing contributions to the material science and design. The high thermal and electrical conductivity, large surface area, mechanical strength, and availability of more mobile electrons make graphene as the suitable anchor group for diverse applications in the field of adsorption of polluted gases, catalyst for the organic conversions, medicinal chemistry, electrochemical sensing, and energy storage devices. Therefore, Graphene oxide (GO) is one of the good choices to develop supercapacitance systems and electrochemical sensing materials. Heteroatom doping, conducting polymer, metal complexes, and metal oxides anchored graphene oxide are more significant because they change the electroactive properties significantly. Considering these, we studied the photophysical and electrochemical properties of chromium and vanadium complex anchored GO that are synthesised by silane and diazonium coupling. The results exhibited that both silane functionalized GO and azo dye enable an electronic interaction due to the recombination of sp^2 and sp^3 states and electron-hole pairs which have extensive importance in developing optoelectronic devices. The chromium and vanadium complex anchored GO showed potential electrochemical sensing properties towards the detection of paracetamol and progesterone respectively. We synthesised and developed two novel nitrogen functionalized GO using nicotinic acid hydrazide (NAHGO) and benzoyl hydrazine (BHGO) for electrochemical sensing of caffeine and supercapacitor applications. Besides, polypyrrole/palladium oxide and zirconia/Multiwalled carbon nanotube

anchored GO for enhanced supercapacitor performances. We used a simple chemical reduction method for nitrogen functionalization, urea based synthesis for ZrO_2 composites, and electrodeposition approach for PdO composites. All the synthesised compounds are characterised for their crystalline structure (Powder X-ray diffraction (PXRD)), chemical bonding (Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy), elemental composition and distribution/mapping (Energy dispersive X-ray spectroscopy (EDX), composition and chemical states (X-ray photoelectron spectroscopy (XPS)) and morphology (Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM)). These results of anchored organic and inorganic compounds demonstrate the excellent structure-property relationship facilitate the interaction between the anchoring and the anchored group that paves the way for electrochemical sensing and energy storage devices.

Keywords

anchoring and anchored group, electrochemical sensor, graphene oxide, supercapacitor

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1. Introduction

The growing worldwide interests in the anchoring graphene based compounds have led us to select the proposed work. It has become increasingly important in recent years and this encompasses a vast range of disciplines and technologies over the next 10 to 20 years. The classical way to improve the property of organic and inorganic compounds is the immobilization especially via carbon materials, silica, clays, organic polymers etc. This is one of the choices made in this study. Here the carbon based supporting material especially graphene framework is selected. This supporting material is highly relevant for energy storage and clean energy compounds. Graphene framework would be the best choice as the supporting material to enhance the surface area, electronic conductivity and suitable morphological properties of anchored compounds.

The potential hydroxyl, epoxy, and carboxyl functional groups on the basal planes and edges of GO offer reactive sites for chemical functionalization through covalent and non-covalent modes [1], [2]. But in the oxidation process, the framework of GO is gravely harmed which results in poor conductivity and thereby restricts its activity as an electrode material [3]. Therefore many approaches have been done to improve the electrochemical properties of GO like the synthesis of GO sheets with layers, preparation of GO with and without defects, chemical functionalization of graphene, and heteroatom doping of GO [4]. Among these, heteroatom doping has become a more promising method since it changes the electrochemical characteristics of GO significantly. The different modifications such as oxygen, nitrogen, sulphur, boron, and phosphorous insertion improve the wettability of the honeycombed lattice of GO and enhance the total capacitance effects and sensing behaviour by redox reactions [5]-[10]. In particular, nitrogen doping has become the centre of attraction since it enhances the electrochemical behaviour of graphene for broad-spectrum applications like the electrochemical sensing, solar cells, oxygen reduction reactions, supercapacitors, and batteries [11], [12]. During nitrogen doping, strong valence bond is formed between nitrogen and carbon because of the small size and five valence electrons of nitrogen [13], [14]. Carbon becomes more positive due to the adjacent electronegative nitrogen atoms and significantly vary the electron donor-acceptor properties of GO [15]. It has already been suggested that the removal or reduction of

the oxygen containing functional groups takes place during heteroatom doping [16], [17]. Nitrogen functionalization of graphene can be done through various methods such as chemical vapour deposition, arc discharge method, segregation growth, and plasma treatment [12]. These methods need more complex and expensive equipment to incorporate nitrogen into the GO framework. Therefore we hope to use organic compounds containing amino groups to perform nitrogen functionalization and the incorporation of nitrogen atoms in the GO framework leads considerable changes or defects in the electronic structure resulting the reduction of GO [18]. In addition, the nitrogen containing functional groups boost the wettability of the electrodes [19]-[21].

As graphene oxide, metal oxides and conducting polymer electrodes have significant supercapacitor applications, the combination of these aspects would generate outstanding electrode materials for energy storage. Based on all these, nitrogen functionalized GO, GO with metal oxides and MWCNT, GO with metal oxides and conducting polymers are synthesised, characterised, and performed electrochemical studies like electrochemical sensing and supercapacitor applications.

2. Literature Review

Some of the relevant literature related to the graphene based compounds for supercapacitors and electrochemical sensors are as follows:

Panahi et al., synthesized, characterized and found out the catalytic activity of N-methyl pyridinamine functionalized graphene oxide for the acetylation of alcohols [22]. Gupta and Saha pointed out the photoluminescence property of intercalated azopyridine graphene oxide [23]. Mondal et al., functionalized and studied the optoelectronic applications of graphene oxide using 2,6-diamino pyridine and Europium [24]. Abney et al., anchored Fe^{3+}, Co^{2+}, Ni^{2+}, or Cu^{2+} graphene oxide hybrid complex with bipyridine and studied its water splitting activity [25]. The oxygen reduction reaction of bioinspired graphene oxide copper complex is studied by Xi et.al., [26]. Sanny Verma et al., synthesised oxovanadium Schiff base on graphene nanosheets and the material catalytic activity showed the heterogeneous catalytic behaviour for the oxidation of alcohols and epoxides [27], [28].

The amine modifications of GO with diisopropylamine, diaminopyridine, dibenzylamine, phenylenediamine, piperidine, phenylethylamine, 2,4-dinitrophenylhydrazine, Bis-(ththalimidoethyl)-amine, and Tris-(hydroxymethyl) methyl aminoethane were also studied [29],[30]. These functionalised compounds of GO exhibit electric double-layer capacitance and pseudocapacitance [19],[31]-[34]. Sujin et al., reported composites of graphene oxide with metal oxides such as SnO_2, MoS_2, Cr_2O_3 by electrodeposition method [35]-[37]. The metal oxides of Fe, Sn, Ni, Mn, V and Co have been utilized with carbon based materials for supercapacitor applications [38]-[40].

3. Research gaps

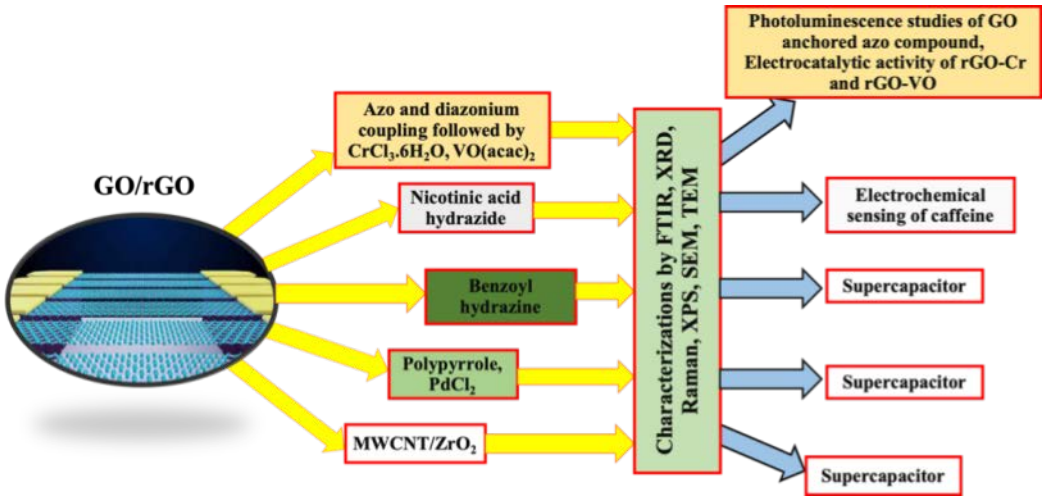
- There are many Cu, Ru, Mo complexes anchored graphene oxide were studied for heterogeneous catalytic applications, adsorption, and CO_2 capture. It is not studied so far for the diazonium ligands anchored on rGO for isomeric switch studies by photoluminescence methods and electrocatalytic applications of the complexes anchored on rGO. Therefore it is important to study the structure-property relationship of chromium and vanadium complex anchored GO for electrocatalytic and their anchored ligands for photoluminescence studies.
- The reported nitrogen functionalization methods of GO are CVD, arc discharge method, hydrothermal treatment, plasma treatment etc. Therefore it is important to develop a simple method for nitrogen functionalization and study electrochemical sensing and supercapacitance properties.
- Electrodeposited PdO/polypyrrole/rGO (PdPGO) and PdO/polypyrrole (PPd) for supercapacitor applications are not reported yet though the binary and ternary composites with various other methods like chemical reduction, hydrothermal treatment, sol-gel method are there for fuel cells, catalysis, and electrochemical sensing applications.
- Urea based hydrolysis method has not been utilized yet for the synthesis of rGO/MWCNT/ZrO_2 composites for supercapacitor applications and the effect of rGO and MWCNT has not compared for the same.

4. Aim and objectives

- To synthesise graphene oxide by modified Hummer's method

- To study the photophysical and electrochemical properties of chromium and vanadium complex anchored graphene oxide (rGO-Cr and rGO-VO)
- To synthesise the nicotinic acid hydrazide anchored graphene oxide (NAHGO) by simple cost effective ultrasonic-assisted chemical route and study the electrochemical oxidation properties of caffeine
- To synthesise and study the supercapacitance behavior of benzoyl hydrazine anchored graphene oxide (BHGO) by simple cost effective ultrasonic-assisted chemical route
- To synthesise electrodeposited binary (palladium oxide/polypyrrole(PPd)) and ternary composites of palladium oxide/polypyrrole/rGO(PdPGO) and study the supercapacitance properties
- To synthesise ZrO_2 composites of MWCNT and rGO and study the effect of MWCNT in rGO/ZrO_2 for the supercapacitance properties

The objectives of the work represents in the flow chart.



5. Importance of the study

The thesis entitled '*Anchored organic and inorganic compounds on graphene framework as materials for sensing and energy applications'* focused on the synthesis of nitrogen functionalized graphene oxide with a simple method, metal oxide composites of GO with electrodeposition and urea based method. This functionalization changes the surface characteristics that lead to the advancement of energy related effects and electrochemical sensing properties of the resultant

compounds. The innovations in the aspects of the design may broaden the industrial importance in the fabrication of energy storage systems and electrochemical sensing devices. This paves the way for an attempt for clean environment and energy.

6. Outline of thesis

The present thesis is titled as '***Anchored organic and inorganic compounds on graphene framework as materials for sensing and energy applications'.*** It is divided into 8 chapters.

Chapter 1 gives the definition of anchored group, allotropes of carbon, an overview of synthesis methods of graphene oxide, properties, different forms of graphene oxide, definition, types, the importance of supercapacitors in one section. The next section presents the review of the graphene oxide anchored materials evolved recently for the various applications in biomedical fields, heterogeneous catalysis, adsorption chemistry especially in electrochemical sensors and supercapacitors. The end of this chapter presents the aim, objectives, and importance of the present study.

Chapter 2 summarizes the different methods and characterisation techniques used for the synthesis and analysis respectively.

In **Chapter 3,** covalently anchored chromium and vanadium complex on reduced graphene oxide (rGO-Cr) is successfully synthesised through trimethoxy silyl propanamine (TMSPA) and phenyl azo salicylaldehyde (PAS) coupling. They are characterised by FTIR, PXRD and SEM-EDAX analyses during the MPhil study. In the present study, we characterised both the chromium and vanadium complex anchored reduced graphene oxide with Raman, XPS, and TEM. This chapter also deals with the photophysical properties of pure PAS and rGO functionalised PAS. The excitation dependent photoluminescence studies of the intermediate ligand trimethoxy silyl propanamine with phenyl salicylaldehyde anchored graphene oxide (rGO-TMSPA-PAS) and phenyl azo salicylaldehyde (PAS) are studied at room temperature according to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition obtained from UV-Visible spectra. Amazing emission properties in the range of 542 nm to 732 nm are observed for functionalized azo dye on graphene oxide through silane coupling (rGO-TMSPA-

PAS) and free azo dye (PAS). The photoluminescence spectra of PAS and rGO-TMSPA-PAS at 282, 368, 372, and 455 nm are shown in **Figure 1** in which PAS showed less emission intensity at 455 nm since some amount of the energy is used for cis-trans isomerisation of PAS. The cis-trans isomerisation of PAS is shown in **Figure 2**.

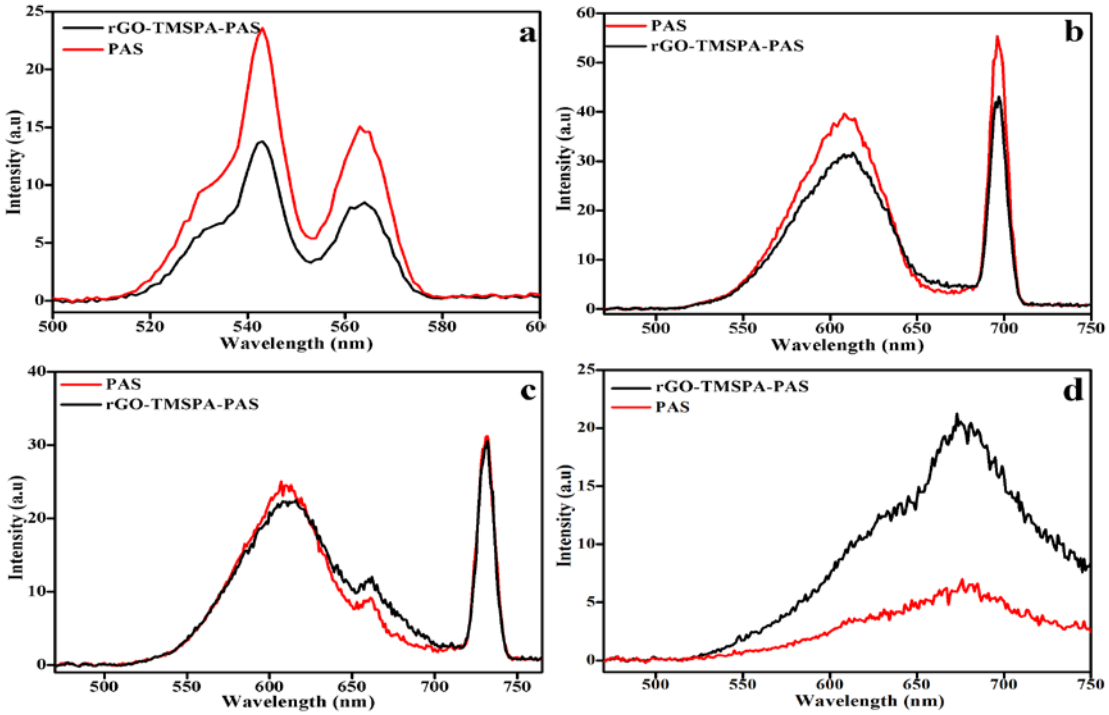


Figure 1. The photoluminescence spectra of PAS and rGO-TMSPA-PAS at (a) 282, (b) 368, (c) 372, and (d) 455 nm

Photoluminescence studies experience a red shift, with a decrease in intensity when the excitation wavelength increases. These results demonstrate that both silane functionalized graphene oxide and azo dye enable an electronic interaction due to the recombination of sp^2 and sp^3 states and electron-hole pairs which have extensive importance in developing optoelectronic devices.

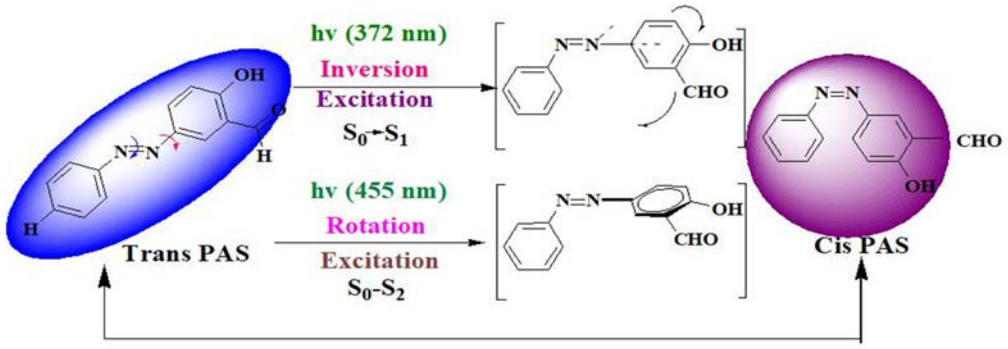


Figure 2. Cis-trans isomerisation of PAS at 455 and 372 nm

Electrochemical studies of the chromium and vanadium complex anchored reduced graphene oxide (rGO-Cr and rGO-VO) are also performed. Electrochemical sensing activity of rGO-Cr is monitored for paracetamol using modified glassy carbon electrode. Cyclic voltammetry measurements indicated that rGO-Cr substantially enhance the electrochemical response of paracetamol. The experimental factors are investigated and optimized. Electrochemical properties of rGO and rGO-VO are also studied towards progesterone using glassy carbon electrode. rGO-VO showed a large surface area and more current than rGO. The parameters such as the effect of pH, scan rate and concentration are also studied for the electrocatalytic reduction of progesterone. The results showed that vanadium complex anchored onto reduced graphene oxide is a promising electrochemical sensor for the detection of progesterone and can be further modified into the fabrication of progesterone detecting devices.

6.1 Findings of chapter 3

- Raman spectra and TEM images showed the distortions of the framework of graphene surface and retention of the sheet structure of rGO after the functionalization of azo and silane functionalized chromium and vandium complex.
- Elemental analysis like XPS is well supported the functionalization of rGO in rGO-Cr and rGO-VO.
- Photoluminescence studies of PAS and rGO-TMSPA-PAS lead to a better route for the solution processable optoelectronics material.

- The rGO-Cr complex showed an enhanced electrocatalytic activity which was utilized for the fabrication of the sensitive electrode for the quantitative detection of paracetamol.
- The electrochemical behaviour of rGO-VO modified glassy carbon electrode in progesterone showed higher current.
- This is due to the contribution of rGO and VO components which has excellent electrical conductivity, high surface area and more interaction sites that directly affects the reduction process of progesterone.

Heteroatom doping has become a more promising method since it changes the electrochemical characteristics of GO significantly. The conventional methods for nitrogen doping of GO are more complex and need expensive equipments. Therefore we used organic compounds containing amino groups to perform nitrogen doping and the incorporation of nitrogen atoms on GO framework leads considerable changes or defects in the electronic structure resulting the reduction of GO. Therefore in chapter 4 and 5 we performed nitrogen functionalization of GO.

Chapter 4 describes the development of a simple modified sensor with nicotinic acid hydrazide anchored graphene oxide (NAHGO) synthesised by ultrasonic-assisted chemical route using hydroxy benzotriazole. Structure and morphologies of NAHGO samples are characterised by Fourier Transform Infrared spectroscopy (FTIR), Powder X-ray diffraction (PXRD), Raman spectroscopy, Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Thermogravimetric analysis (TGA). These characterisations support the nitrogen functionalization and reduction of GO. Morphology modification of the material provided the route for the more electroactive surface that influenced the electrooxidation of caffeine with increased current. We demonstrated the electrochemical behaviour of NAHGO on glassy carbon electrode (GCE) for caffeine detection by employing voltammetric techniques. The influence of scan rate, pH, and concentration on the peak current of caffeine is also studied. The detection limit determined was 8.7 nM, the best reported so far. The NAHGO sensor is employed for the determination of caffeine in '*Imol plus'* and '*energy drink'*. The results showed that NAHGO modified electrode is one of the best preferences to establish new,

efficient and reliable analytical tools. The detection of caffeine using differential pulse voltammetry and its electrochemical oxidation is shown in **Figure 3**.

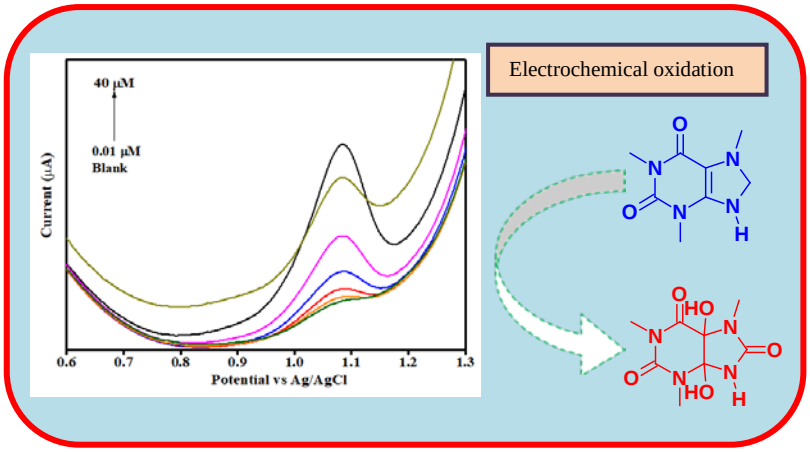


Figure 3. The detection of caffeine using differential pulse voltammetry and its electrochemical oxidation

6.2 Findings of chapter 4

- The synthesis and properties of NAHGO for electrochemical detection of caffeine was discussed. Structure and morphologies of NAHGO were studied by IR, PXRD, Raman, XPS, SEM and TGA.
- The electrochemical oxidation of NAHGO towards the alkaloid, caffeine was analyzed. NAHGO displayed enhanced electrochemical activity towards the quantitative determination of caffeine with improved detection limit of 8 nM.
- The NAHGO sensor was also employed for the determination of caffeine in '*Imol plus'* and '*ocean one 8'* energy drink.

Chapter 5 illustrates the synthesis of benzoyl hydrazine anchored graphene oxide (BHGO) using graphene oxide (GO) and benzoyl hydrazine (BH) via a simple, cost-effective ultrasonic-assisted chemical route. It is represented in **Figure 4**.

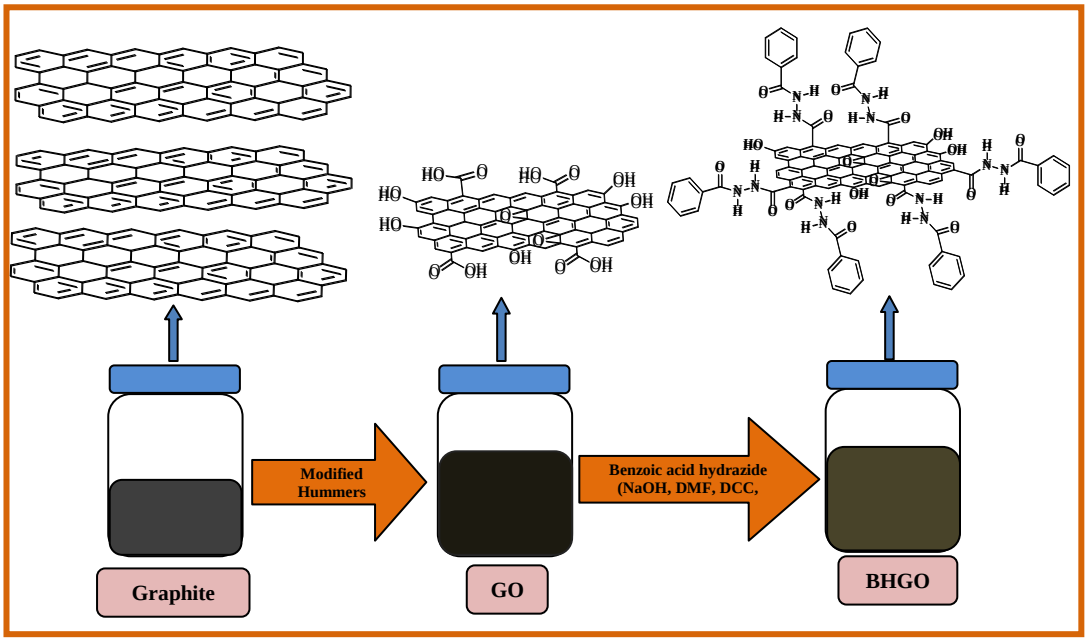


Figure 4. Synthesis of benzoyl hydrazine anchored on GO (BHGO)

BH acted as a nitrogen source, reducing agent, and morphology modifier resulting in good electrochemical performance of BHGO. The supercapacitor behaviour of BHGO is investigated in different aqueous electrolytes and it exhibits a specific capacitance of 170 F g^{-1} at a current density of 1 A g^{-1} in 1 M H_2SO_4 and capacitive retention of 85 % over 5000 cycles at 5 A g^{-1}. **Figure 5** represent the CV curves of BHGO in 1M of Na_2SO_4/KCl/H_2SO_4 at 30 mV s^{-1}, GCD curves of (b) BHGO in 1 M KCl/Na_2SO_4/H_2SO_4 at 1 Ag^{-1}, (c) BHGO in 1M H_2SO_4 at current densities 1 to 3 A g^{-1}, (d) Relation of specific capacitances with current densities for BHGO, (e) Nyquist plot of BHGO in different electrolytes, and (f) Cyclic stability and coulombic efficiency of BHGO in 1 M H_2SO_4 at 5 A g^{-1}.

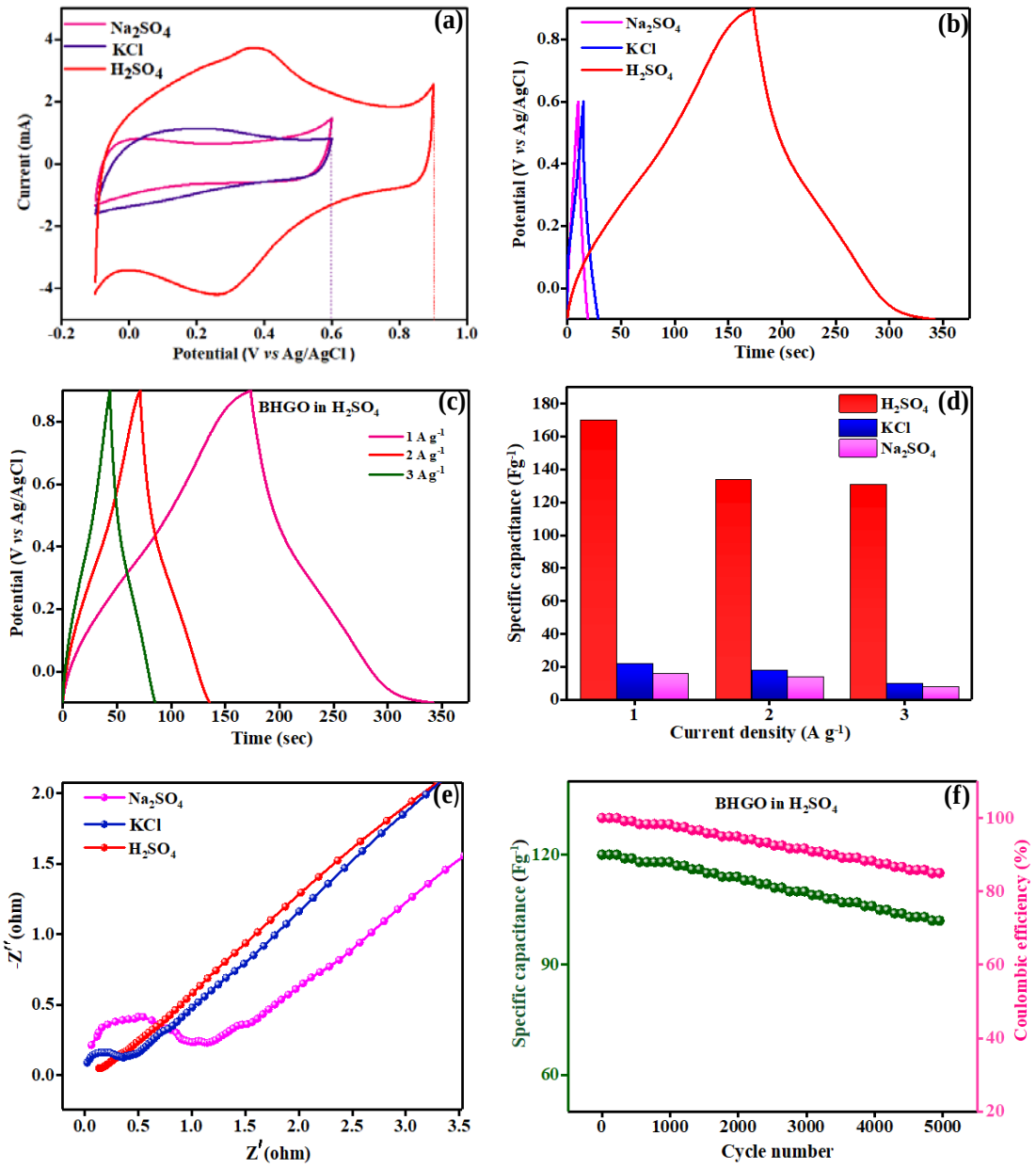


Figure 5. CV curves of BHGO in 1M of Na_2SO_4/KCl/H_2SO_4 at 30 mV s^{-1}, GCD curves of (b) BHGO in 1 M KCl/Na_2SO_4/H_2SO_4 at 1 Ag^{-1}, (c) BHGO in 1M H_2SO_4 at current densities 1 to 3 A g^{-1}, (d) Relation of specific capacitances with current densities for BHGO, (e) Nyquist plot of BHGO in different electrolytes, and (f) Cyclic stability and coulombic efficiency of BHGO in 1 M H_2SO_4 at 5 A g^{-1}

This high performance is attributed to the enrichment of electroactive sites of GO through nitrogen moieties enhancing faradic redox reactions and thereby the polarization at the electrode surface.

6.3 Findings of chapter 5

- Benzoyl hydrazine anchored GO was successfully synthesised by a simple ultrasonic-assisted chemical route.
- This work embodies the enrichment of electroactive surfaces of GO with the nitrogen moieties. The anchoring of BH on the surface of GO is confirmed by the spectroanalytical methods like FTIR, XRD, Raman, XPS, SEM, and TGA.
- The supercapacitive *behaviour* of BHGO is studied in different aqueous electrolytes 1 M KCl, Na_2SO_4 and 1 M H_2SO_4 .
- The outstanding performance in 1 M H_2SO_4 is ascribed to the highest molar ionic conductivity and the smallest ionic radius of H^+ ion.
- The calculated specific capacitance of BHGO in 1 M H_2SO_4 is 170 F g^{-1} at a current density of 1 A g^{-1} which is five times higher than that of GO and hundred fold superior to BH.
- The BHGO exhibits pronounced stability with 85 % capacitance retention even after 5000 cycles at a current density of 5 A g^{-1}.
- Hence, this method offers a good prospect in the development of advanced energy storage materials.

Various transition metal oxides (RuO_2, MnO_2, CeO_2, V_2O_5 and Fe_3O_4) have been used as electrode materials to store charge by fast and reversible reactions. The high electrical resistance and poor electrochemical reversibility of the metal oxides have limited their energy storage capacity for practical uses. The mixed oxide composites have excellent electrochemical behaviour to cater the cycling stability and the specific capacitance compared to the single metal oxide characterized with poor cyclic stability. Therefore, chapter 6 and 7 deals with the combinations of GO metal oxide composites for supercapacitor applications.

Chapter 6 explains the novel electrodeposited palladium oxide-polypyrrole (PPd) and its ternary composite with reduced graphene oxide (PdPGO) to attain excellent electrochemical properties and high stability. **Figure 6** represents the synthesis and electrochemical behaviour of PdP and PdPGO.

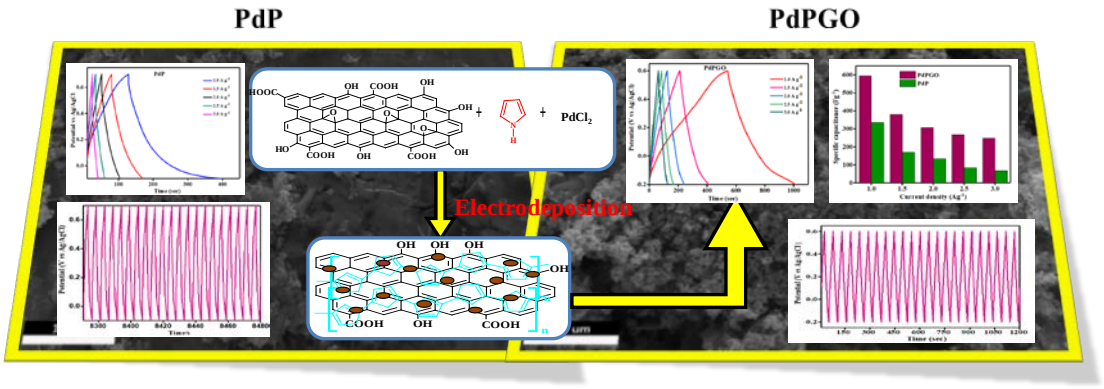


Figure 6. Synthesis and electrochemical behaviour of PdP and PdPGO

The electrodeposited PdPGO and PPd composites on stainless steel bestow superior electrochemical properties and specific capacitance of 595 F g^{-1} and 335 F g^{-1} at 1 A g^{-1} in 1 M H_2SO_4. The comparison of galvanostatic charge-discharge studies of PPd and PdPGO are represented in **Figure 7**.

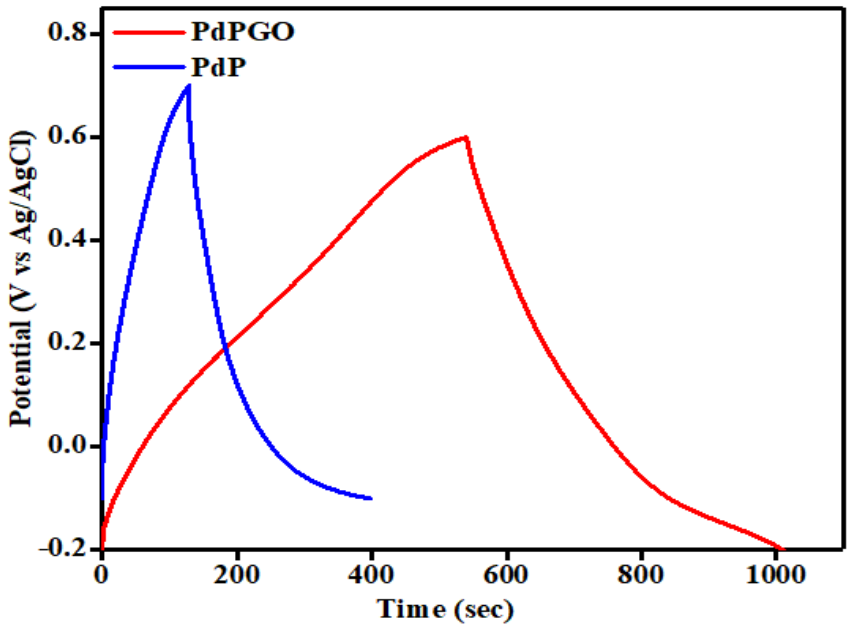


Figure 7. Comparison of galvanostatic charge-discharge studies of PPd and PdPGO

The closely packed rGO with PdO nanoparticle embedded in the PPy matrix prevents the aggregation of rGO layers which is responsible for the enhanced electrostatic interactions at the electrode-electrolyte interface in PdPGO. Outstanding supercapacitance retention of 88 % even after 5000 cycles at 5 A g^{-1} is attained for the

ternary composite of Pd. These profound electrochemical characteristics indicate the synergic effect between the appropriate proportions of conducting polymer PPy, PdO nanoparticles and the highly electrically conductive rGO makes easy diffusion of ions results in a promising material for supercapacitors with high cyclic stability.

6.4 Findings of chapter 6

- A novel ternary composite of PdPGO was prepared by electrodeposition method using chronoamperometry.
- The structural and morphological studies such as FTIR, XRD, Raman, XPS, SEM, EDX mapping, and TEM signify the correlated properties for the improved electrochemical performance of the composites.
- The PdPGO demonstrated the specific capacitance of 595 F g^{-1} at a current density of 1 A g^{-1} in 1 M H_2SO_4 and outstanding stability with 88 % retention over 5000 charge-discharge cycles at a current density of 5 A g^{-1}.
- The good specific capacitance performance of PdPGO which is seven times greater than that of PPy (91 F g^{-1}), thrice that of PPy-rGO (200 F g^{-1}) and higher than that of PdP.
- The synergic effect of its individual components, charge transfer features of PPy and PdO, an electroactive network of rGO at the electrodes turns out PdPGO to be a potential and promising electrode with the outstanding electrochemical performance for the future.

In **Chapter 7**, the novel zirconium based composite of graphene oxide and multiwalled carbon nanotubes (rGO/MWCNT/ZrO_2 (GMZ)) is synthesised by urea based hydrolysis method and studied the electrochemical properties as a supercapacitor. To understand the effect of MWCNT in the rGO/MWCNT/ZrO_2 composites, rGO/ZrO_2 (GZ) and MWCNT/ZrO_2 (MZ) were also synthesised using the same conditions. **Figure 8** represents the synthesis and electrochemical behaviour of

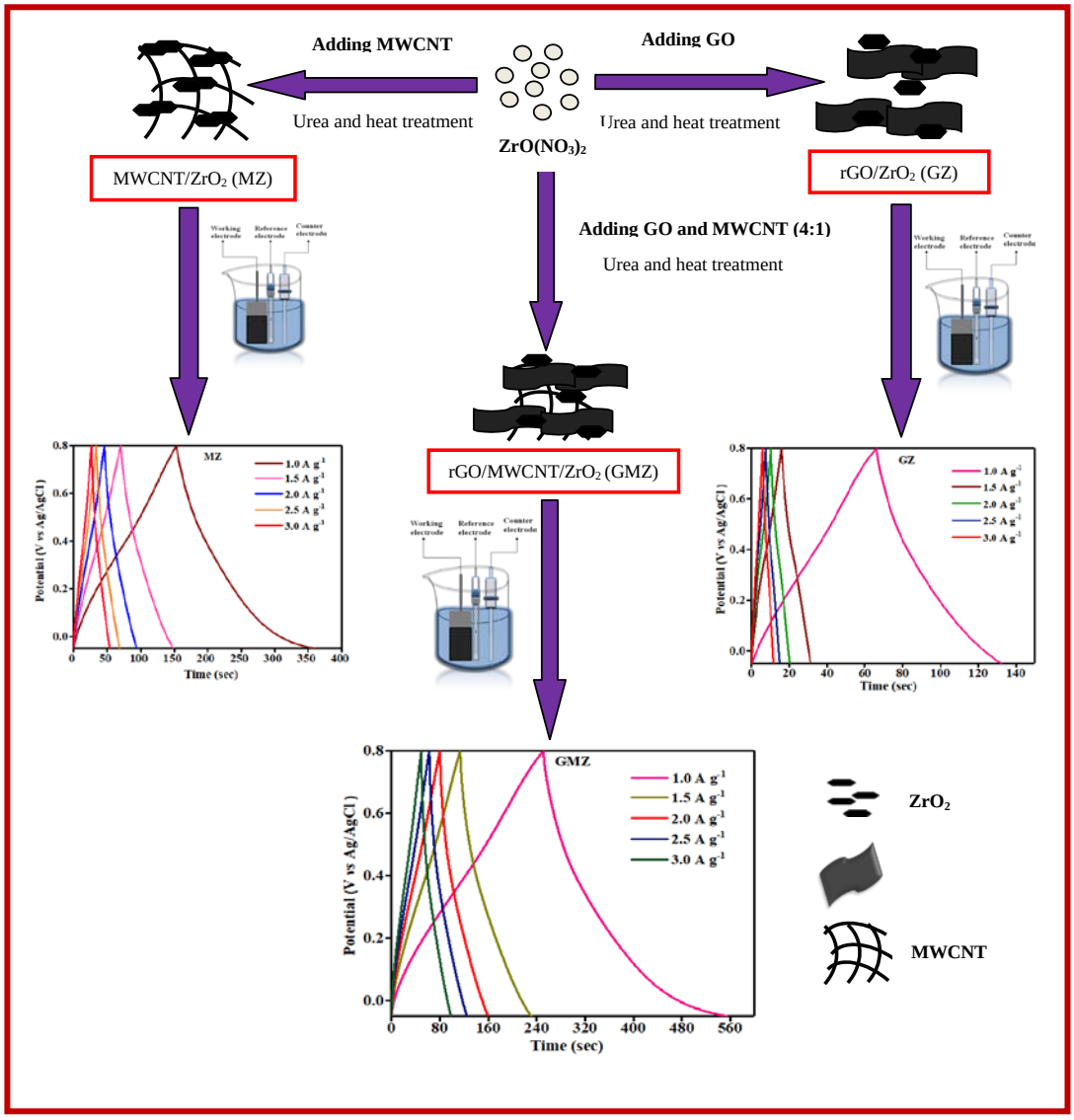


Figure 8. Synthesis and electrochemical behaviour of MZ, GZ, and GMZ composites.

MZ, GZ, and GMZ composites. The structure and morphology of rGO/MWCNT/ZrO_2, rGO/ZrO_2, and MWCNT/ZrO_2 composites were characterised by Fourier transform infrared spectroscopy (FTIR), Powder X-ray diffraction (PXRD), Scanning electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The supercapacitance behaviour of the rGO/MWCNT/ZrO_2, rGO/ZrO_2, and MWCNT/ZrO_2 composites was investigated through cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The specific capacitance of rGO/MWCNT/ZrO_2 is obtained as 357 F g^{-1} which is higher than that of 242 F g^{-1} of MWCNT/ZrO_2 and 86 F g^{-1} of

rGO/ZrO_2 at current density of 1 A g^{-1}. **Figure 9** presents the bar diagram of specific capacitances of GZ, MZ, and GMZ in different current densities.

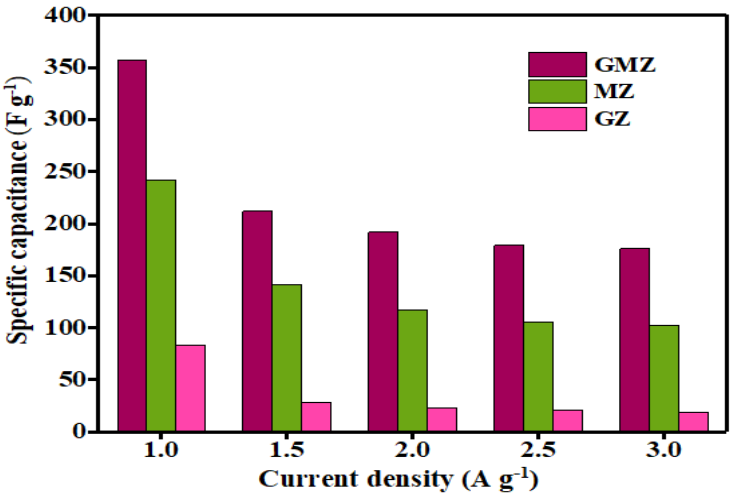


Figure 9. Relation of specific capacitances of GZ, MZ, and GMZ in different current densities.

In GMZ, 98 % of specific capacitance is retained even after 4500 cycles at 5 A g^{-1}. The highest specific capacitance of rGO/MWCNT/ZrO_2 is because of the small size of ZrO_2 which is shown in **Figure 10** and the small addition of MWCNT which prevents the restacking of rGO layers in the ternary composite.

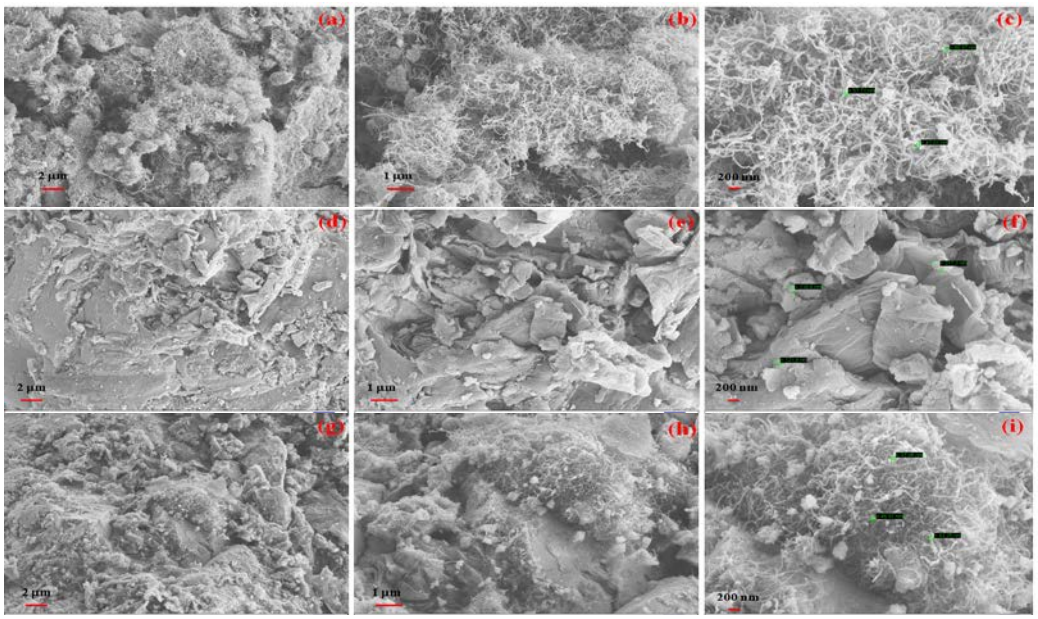


Figure 10. SEM images of MZ (a-c), GZ (d-f), and GMZ (g-i). The size of ZrO_2 in MZ, GZ, and GMZ are 41 to 57, 118 to 211, and 37-46 nm respectively.

6.5 Findings of chapter 7

- A novel flexible 3D ternary architecture of MWCNT supported rGO/ZrO_2 electrode has been designed and fabricated by hydrolysis method.
- The anchoring of MWCNT on graphene effectively reduces the degree of restacking of graphene sheets and enhances the surface area utilization efficiency.
- The GMZ electrode exhibited remarkable supercapacitive performance with a high specific capacitance of 357 F g^{-1} at a current density of 1 A g^{-1}.
- Pronounced cycling life of GMZ 5000 cycles in 1 M H_2SO_4 aqueous electrolyte solution.
- This approach is highly relevant to achieve commercial supercapacitors supporting portable energy storage devices.

Chapter 8 presents the conclusion and suggestions for future research.

- Successfully anchored organic and inorganic compounds on graphene oxide.
- The research study comprises of the synthesis of chromium and vanadium complex anchored GO, nitrogen doped graphene oxide, PdO, ZrO_2 composites of rGO.
- The photophysical and electrochemical properties of the compounds were studied in detail for sensing and energy applications.

The future directions are

- The vanadium and chromium complex anchored GO can be extended for different metal complexes for applications such as CO_2 capture, adsorption studies, heterogeneous catalysts for organic functional group conversions.
- Nitrogen functionalized GO can be done with various metal nanoparticles, metal oxides for supercapacitor, electrochemical sensing applications.

- The PdPGO and MWCNT/rGO/ZrO_2 study can be done for other bimetallic oxide combinations for supercapacitor and electrochemical sensing applications.

7. Conclusion

The research study is about the photoluminescence studies of PAS and rGO-TMSPA-PAS, electrocatalytic properties of rGO-Cr and rGO-VO, synthesis of nitrogen functionalized graphene oxide, PdO, ZrO_2 composites of rGO. The photophysical and electrochemical properties of the compounds were studied in detail by spectroscopic and electrochemical techniques.

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List of Publications and presentations

Publications

J. Jose, P.B. Sreeja, *Spectrochemical and theoretical approaches for acylhydrazone-based fluoride sensors,* Res. Chem. Intermed. 45 (2019) 425-435

J. Jose, A.R. Rajamani, A. Sreekanth, S.P. Jose, P.B Sreeja, S.C. Peter, *Photophysical and Electrochemical Studies of Anchored Chromium (III) Complex on Reduced Graphene Oxide via Diazonium Chemistry,* Appl. Organomet. Chem. 33 (2019) e5063.

J. Jose, S. Giridharan, P.B Sreeja, *Electrochemical Detection of Dissolved Sulphur Dioxide Using Bovine Serum Albumin - Theoretical and Experimental Approach,* Orien. J. Chem. 35 (2019) 1182-1186.

A.M John, J. Jose, R. Thomas, K.J Thomas, P.B. Sreeja, *Spectroscopic and TDDFT investigation of highly selective fluoride sensors by substituted acyl hydrazones,* Spectrochimica Acta Part A. 236 (2020) 118329

Presentations

Participated International Conference on Chemistry and Physics of Materials (ICCPM-2018) held in St Thomas College Thrissur on December19, 20 & 21 and presented paper in *"Preparation and Electrochemical performance of grafted Oxovanadium complex on graphene oxide"*.

Participated ICCON 2019 held in SRM Institute of Science and Technology on Jan 28,29 & 30 and presented paper in *"Synthesis and Photoluminescence properties of grafted azo dye on graphene oxide"*

Participated and presented paper entitled *"Anchored vanadium complex on RGO via Diazonium Chemistry: Potential Photochemical Catalyst"* (ACC-2019) held in Dubai, U A E

Presented paper entitled "*Synthesis of Anchored Nicotinic Acid Hydrazide Graphene Oxide for Efficient Electrochemical detection of Caffeine* in an International Conference on Frontier Areas in Chemical Technologies-2019 held at Alagappa University, Karaikudi

Participated 11th Bengaluru India nano held in Bengaluru on March 2-4 2020 and presented paper in *"Anchored aminobenzoic acid hydrazide on graphene oxide, synthesis, Characterization and evaluation of the electrochemical response of progesterone"*